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INVESTIGATION OF TREATING ELECTRO-PLATERS CYANIDE WASTE BY ELECTRODIALYSIS

Sidney B. Tuwiner

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ABSTRACT

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These concentrations are maintained by the use of electrodialysis to transport cyanides continuously from the second rinse solution back to the first rinse solution and also from the first rinse back to the plating bath. In this way, all cyanide is recovered and returned to the bath. Design parameters are determined from the experiments of this study and costs are estimated.

The experimental system used in this study was a prototype of a commercial size electrodialysis unit operated continuously under conditions which simulated those of the projected two-stage commercial system using a cyanide copper plating bath.

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SECTION I

CONCLUSIONS

The experimental work was performed on a simulated cyanide copper plating bath. The conclusions reached are considered applicable to cyanide baths of zinc, cadmium, silver and gold.

1. An 8 cell-pair stack, with 12.8 sq ft of total effective membrane surface, was successfully operated continuously for one week. Cyanide was recovered from a simulated rinse solution containing 406 mg/l of cyanide by returning it to a simulated plating bath containing 52,100 mg/l. A simulated dragout rate of 0.87 gallons per hour was employed, furnishing the cyanide which was recovered.

2. The stack successfully maintained the same concentration ratio, of 128:1, between solutions of lower concentration simulating a first and second rinse. Thus in a two stage rinse system with two electrodialysis stacks, assuming the same ratio of 128:1, the second rinse would contain 3.2 mg/l of cyanide.

3. Such a two stage system, with a total effective membrane area of 25.6 sq ft, is capable of handling a dragout of 0.87 gph without the discharge of rinse solution.

4. Essentially all cyanide and metal values are returned to the plating bath or to a solution of comparable concentration. Electrolyte impurities are returned also and are consequently accumulated. The bath requires, therefore, either periodic or continuous withdrawal and replacement, or periodic or continuous purification. The requirement of withdrawal or purification depends on the conditions of the plating system and on the limits of impurity concentrations which are tolerated.

5. The handling and treatment of rinse waters is automatic and self-regulating.

6. The membranes, Ionac MA3475 and MC3470, 10 mils nominal thickness, showed no evidence of deterioration after 800 hours of operation. Experience from application of these membranes to other alkaline systems suggests a life expectancy of from one to several years.

7. The system requires 30 sq ft of total effective area for each gph of bath dragout when the final rinse concentration is 1/16,500 of that of the bath concentration.

8. The stack which was used in this study included no separate electrode cell rinse solutions. There was consequently a deposit of metallic copper on the cathode. This deposit had to be removed after stack operation of one week.

9. For a typical small plating establishment with 1 gph of bath dragout, the manufacturing cost of the electrodialysis system is $1,600, exclusive of rinse vessels, installation and space requirements.

10. The total power requirement for this capacity is 4 KW for rectifier and pumps, based on 6 volts per cell-pair for the stack.

11. The maximum concentration at which the cyanide may be recovered is about 11.5 oz/gal of copper cyanide with an appropriate concentration of about 13 oz/gal of sodium cyanide. The reason for this limitation is the transport of water, together with that of ions, in electrodialysis. If the plating bath contains 16 oz/gal of copper cyanide and 18 oz/gal of sodium cyanide,the return of the cyanide and copper values requires an evaporation of 0.4 gallons for each gph of dragout. Normally the plating solutions which are from 50-70°C suffer evaporation losses which are in excess of this amount.

12. When the cyanide plating bath contains brighteners which are anionic substances of high molecular weight, some special provision is required to avoid membrane fouling.

SECTION II

RECOMMENDATIONS

It is recommended that a second phase be undertaken to design a modular unit for small to medium size plating shops and to provide a demonstration and evaluation of the system in a typical shop.

The stack design should provide for two stages combined in a single stack, with internal stream flow between stages. The design of the manifolds, frames and spacers used in commercially available equipment should be modified to provide greater simplicity, insurance against internal leakage and greater volume of solution flow than is now possible with the Aquachem WD6-2 unit. This will optimize capacity and efficiency and eliminate all but routine scheduled maintenance. Provision should be made in the design modification for removal and replacement of cathodes without breaking the remainder of the stack assembly.

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SECTION III

INTRODUCTION

Cyanide waste constitutes a major source of pollution. Under Federal "drinking water standards" for cyanide, the recommended maximum concentration is 0.01 ppm, and 0.2 ppm is considered the level for rejection. This standard has served as a guideline for the states and municipalities, most of which have adopted limits ranging from 0.05 to 1 ppm.[1]

There are at least 20,000 plating establishments in the U.S.,[2] most of them involved with one or more cyanide plating operations, and most of them are very small. Among the major industries discharging cyanide-bearing wastes, aircraft engines and parts account for 293,760 gpd,[3] missile parts 32,000 gpd at 80 ppm,[4] instrumentation 13,000 gpd,[5] electronic hardware 259,000 gpd at 200-1500 ppm,[6] home appliances 108,000 gpd,[7] television antennae 11,000 gpd,[8] silverware 165,000 gpd at 172 ppm,[9] automobile manufacture 410,000 gpd at 204,[10] and "unspecified," 250-400 gpd at 40-130 ppm.[11]

Cyanide at a concentration of 0.05 ppm is fatal to many species of fish and other marine life.[12] In municipal biological sewage treatment plants, a concentration of 1-2 ppm of copper cyanide is detrimental, affecting activated sludge formation adversely.[13]

All cyanide wastes may be treated with one or another form of available chlorine for conversion of the cyanide to cyanate or for its complete destruction. The latter requires a holding time of 24 hours.[14] Metallic elements associated with the cyanide are converted to precipitates of the hydroxides or basic salts. To reduce the metal content of the treated water to permissible concentration levels it is necessary to clarify the effluent. It may be necessary also to remove excess chlorine and to neutralize.

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Chlorination is relatively expensive in equipment and reagent costs as well as in labor for control and monitoring. It requires 7 to 9 lbs available chlorine per lb cyanide.[14] Chlorination with chlorine gas is practical only in large installations. Usually it is preferable to chlorinate using calcium hypochlorite (70 per cent as available chlorine). The cost of this reagent is about 35 cents per pound of available chlorine, or about $3 per pound of cyanide.

An alternate method, requiring about 3.5 lbs available chlorine per pound cyanide, is to chlorinate only to the extent of converting cyanide to cyanate at pH 10.0. The pH is then reduced to 3.5 and held for at least 5 minutes to hydrolyze the cyanate. The control procedure for this method is much more demanding than for complete chlorination.[15] Cyanide values are lost in both methods and metal removal is very costly.

Other methods, involving evaporation of rinse solutions, have been used or proposed. These eliminate the need for chlorination but require even more expensive equipment for evaporation, condensation and steam generation. The simplest and oldest of these methods involves a two-stage rinse, first in a "still" rinse and finally in a "running" rinse. Periodically the still rinse solution is concentrated by evaporation and returned to the plating bath. Still rinse solution which is withdrawn to the evaporator must be replaced with water.

Although most of the dragout of cyanide is recovered in this method, there is a portion which is discharged from the running rinse solution. A more satisfactory approach to abatement of cyanide pollution is represented by the evaporative system which ideally recovers all of the cyanide and metal values at the expense of considerable installation and operating costs. This is discussed on pages 31-33.

The evaporation system is more expensive than chlorination for treating cyanide waste, except where the values

recovered represent a substantial credit as is the case in cyanide cadmium and precious metal baths in larger plating establishments.

Electrodialysis is an industrial process in which ions are transported from one to another solution while under the influence of an electric field imposed across membranes which separate the solutions. The commercial equipment which provides the solution flow channels, membranes, cells and electrodes is called a stack.

Commercial stacks differ from one another in numerous details but all of them bear some resemblance to a filter press with the membranes corresponding to filter cloths and with spacers corresponding with the filter press frames. There are also flow manifolds for the two solution streams in electrodialysis, and ports connecting these manifolds with the cells which are defined by the membranes and separators. There are two types of cells which alternate in sequence; one is for the solution which is being diluted by the transport and the other is for the solution which is being concentrated. The port connections are designed to provide communication of each cell with the appropriate pair of solution manifolds, one of them for the feed and the other for the product solution. Thus there are four solution manifolds for each stack.

A stack includes end plates similar to those of a filter press, and some means, such as a frame or tie rods, for compressing the stack components between these plates. This provides for ease of assembly and disassembly for cleaning or replacement of membranes or other stack components. When the stack is in operation these are held in compression to insure against leakage internally between the two solution streams, or externally from between the frames.

There are several points of difference between an electrodialysis stack and a filter press. The space in the cells between the membranes is occupied by plastic separators,

which serve to prevent physical contact between the membranes of each cell. These separators are foraminous in construction so that there is a minimum of area of membranes which is blanked out or covered and so that there is the least obstruction to the flow of ionic current across the cells.

The details of stack construction and the principles of this method have been exhaustively described and discussed elsewhere.[16] Two types of membrane are used, one of them is cation-selective while the other is anion-selective. They alternate in sequence and each pair defines either a concentrating or a diluting cell, depending on the direction of the electric field in relation to the order of the membrane sequence.

Thus the electrical field is induced by the end electrodes of the stack and the ionic current flows from one electrode to the other along all of the cells in series. With respect to solution flow the cells are in parallel between each manifold of the pair for each of the solution streams.

Except in the end cells, each bounded on one side by an electrode, the only electrochemical process is that of ion transport through the solutions and across the membranes. Electrolysis occurs in these end cells. Most often in commercial electrodialysis, solution streams are circulated through these end cells which are apart from and in addition to the two main solution streams through the other cells. This is done to separate the products of electrolysis from the contents of these main streams. This separation requires additional pump and circulation means for the so-called electrode rinse streams.

In all of the cells anions are transferred through anion-selective membranes while cations move through cation-selective membranes. Both types of ions are driven by the electrical field in opposite directions. By virtue of ion-selectivity of the membranes there is an accumulation of electrolyte in one group of cells, the concentrate stream cells, and a depletion in the other, the diluting stream cells

The degree of ion-selectivity, expressed as a ratio of the current carried by the favored ions to the total current through a membrane, may vary up to unity for perfect ion-selectivity. In this case of a perfect membrane the transfer of each gram equivalent of electrolyte requires precisely one faraday of current for each membrane-pair in the stack. This would represent a current efficiency of 100 per cent. In practice membranes are never perfectly ion-selective. Some of the current is therefore carried by counter-ions moving in the direction opposite to that of the preferred ions. The effect of membrane ion-selectivity on current efficiency is expressed by the following:

$$E = t_a + t_c - 1$$

where E is the current efficiency as a fraction, and t_a and t_c are the ion selectivities of anion-, and cation-selective, membranes, respectively.

Current efficiency is an important parameter in an evaluation of an electrodialysis system inasmuch as it is closely related to unit power consumption as well as to unit membrane capacity. Inasmuch as the current efficiency is a function of the ion-selectivities of both anion- and cation-selective membranes, it is impossible to assign values to these individually. However, in a solution containing polyvalent complex cyanide anions it is likely that a very low current efficiency is ascribable to the "poisoning" effect of these ions on the anion-selective membranes.

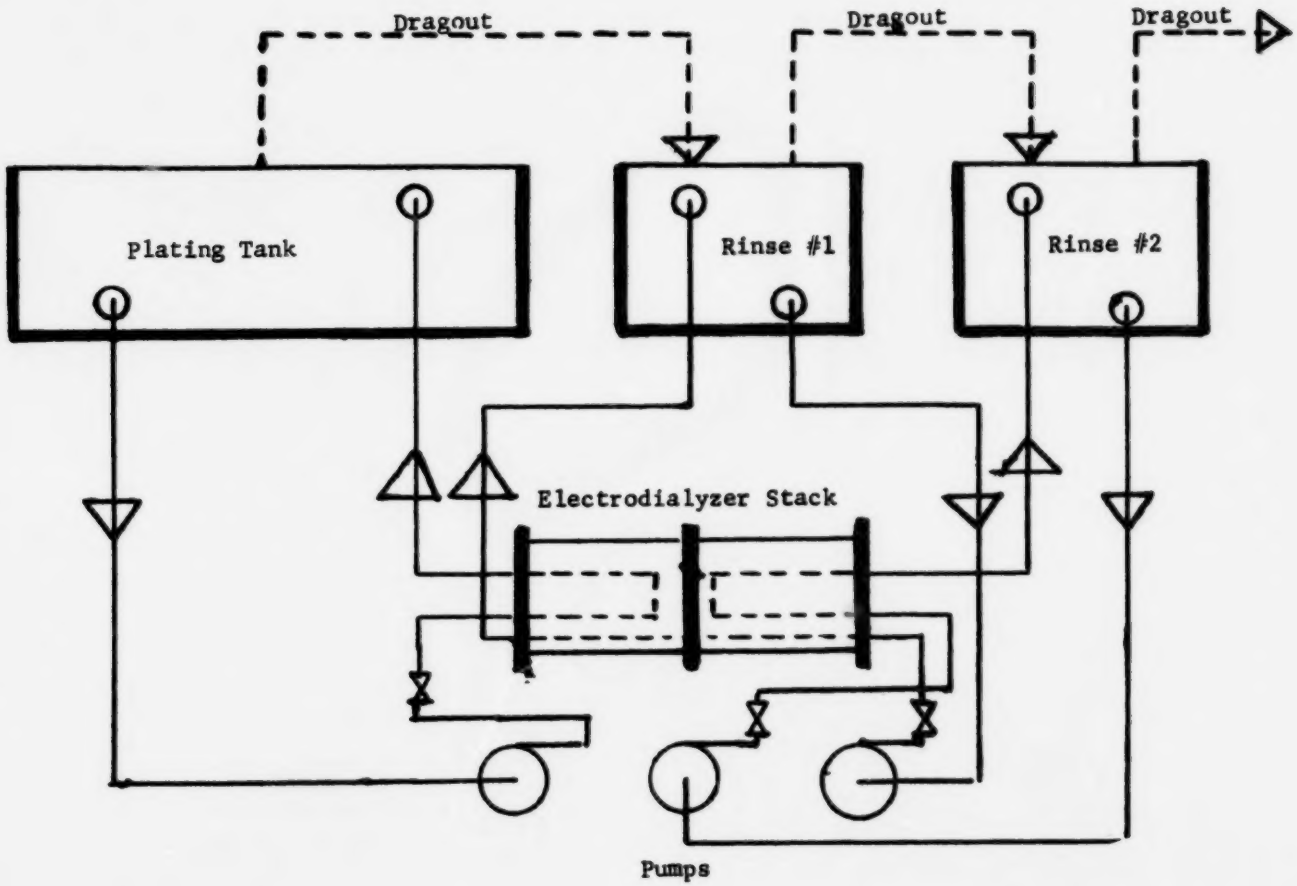
De Korosy[21] has presented experimental data which indicates that polyvalent anions, including complex cyanides, may be immobilized in the membrane polymer and may promote the backward electromigration of cations. There was some concern lest this propensity might limit the concentration ratio and also the current efficiency. On the other hand it is known that the metal and cyanide values in rinse solutions from the cyanide leaching of copper concentrates and gold ores are recoverable by electrodialysis and that a patent[18] has issued in which this is claimed.

There have been still other proposals to recover cyanide from waste rinse streams by electrodialysis. These have been economically unsuccessful, or at best of marginal utility because such proposals have been for multistage removal of cyanides from an existing effluent stream. Since each stage in electrodialysis can conveniently remove at best not more than about one-half of the cyanide in the entering stream, the number of stages required to bring the effluent to acceptable levels of cyanide concentration is prohibitively great. On the other hand, treatment of the stream in only two or three stages, followed by chlorination serves only to complicate the system. Especially for smaller establishments, the system must remain simple if it is to be practical.

The present investigation was initiated to apply electrodialysis to a rinse system, so that compositions of the rinse solutions are maintained and the cyanide and metal values are returned and recovered. The basis of the study is a concept, illustrated schematically in Figure 1, in which electrodialysis is incorporated within the rinse system in such a manner that the transport of electrolyte in each stage of electrodialysis is precisely equal to the transport of electrolyte in the opposite direction by drag-out. According to this concept the combined system ideally is closed and there is no discharge of solution nor any requirement for plating solution makeup. Practically this ideal is not fully achieved owing to accumulation of impurities and the requirement of some evaporation and compensating water addition in the case of highly concentrated plating solutions.

FIGURE #1

COMMERCIAL SYSTEM CYANIDE RECOVERY



SECTION IV

EXPERIMENTAL

The electrodialysis stack, power supply, solution storage containers, tubing connections, pumps, flowmeters, and electrical instruments are components of Aqua-Chem Model WD 6-2, Aquachem Division, Coca Cola Inc., Waukesha, Wisc.

The solutions are stored in two plastic bottles, each of 5 gallon capacity, one holding the concentrating stream solution, the other holding the diluting stream solution. Each bottle is provided with a bottom discharge nipple and hose connection to one of two circulation pumps. Each pump circulates a flow through a rotometer and the electrodialyzer stack. A hose connection from the stack leads the stream back to the storage bottle.

Each stream circulates continuously between the storage vessel and the stack. Within the stack the two streams are separated by the membranes. Transfer of the stream components is negligible until the electric current is applied. This current is maintained continuously, effecting a proportionate rate of electrolyte transfer.

The dragout is simulated by means of a constant displacement pump discharging a portion of the concentrated stream from the storage bottle to the diluting stream which it enters through the side arm of a "tee" connection in the line which returns the diluting stream from the stack. There is provision for an overflow from the diluting stream storage vessel to the concentrating stream. Volume changes of the two solutions are observed and measured to determine the electroosmotic flow rates under controlled experimental conditions. Provision is also made for representative sampling of both solutions.

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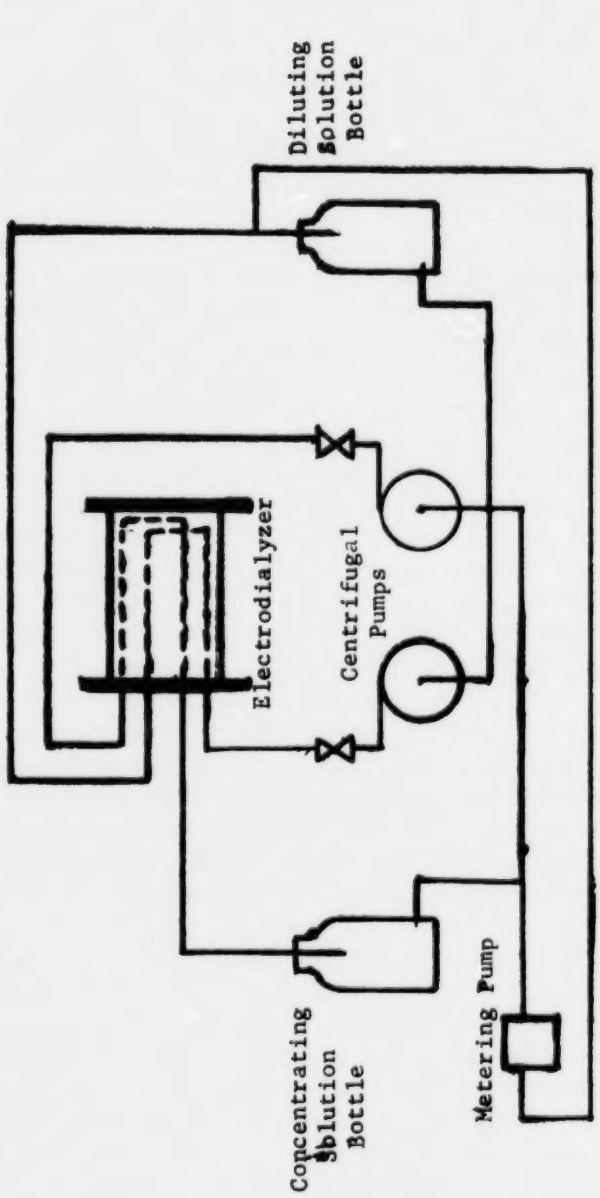
FIGURE #2

LABORATORY SYSTEM



The composition of the bath used in this investigation is as follows:

Copper Cyanide	16 oz/gal	120 gpl
Sodium Cyanide	18 oz/gal	135 gpl
Sodium carbonate	2 oz/gal	15 gpl
Sodium hydroxide	4 oz/gal	30 gpl

This bath is typical of those employed for heavy copper plating.[19] For improved speed and plating quality, the bath is maintained at about 145°F. At the normal bath temperature, the evaporation rate is about 5 gallons for each sq ft of exposed bath surface in 24 hours. Some water transport accompanies the cyanides when using electrodialysis to recover them from the rinse. From the very dilute solution of the second rinse, this electroosmotic flow of solution is far less than the dragout rate, and the effect on the water balance of the system is consequently very slight; but, from the first rinse to the plating bath the electroosmotic flow may exceed the dragout rate.

Specifications of the Aqua-Chem WD 6-2 electrodialysis stack are as follows:

Number of Cell-Pairs	50
Effective Area per Membrane	0.8 sq ft
Rated Flow, Concentrating Stream	600 gal/hr
Rated Flow, Diluting Stream	600 gal/hr
Per cent removal, NaCl	5-7%
Stack voltage	50-120 volts
Concentration, NaCl	Up to 4%

In this study the number of cell-pairs was reduced to eight. This reduced the rated flow proportionately for both streams. The flow rate in these experiments was actually approximately three times the manufacturer's rating and the removal of cyanides was, under optimum conditions, as high as 50 per cent when the stack was operated at 50 volts compared with the rated 5-7 per cent for sodium chloride.

This indicates an approximate ten-fold increase in unit capacity from that which is normally assumed as a basis for design. It suggests also that an even greater increase in unit capacity may be possible if the stack components are redesigned for a greater flow rate.

The experimental data was obtained under steady state conditions. This required no more than 30 minutes for attainment after a change in one of the system parameters. Constancy of solution composition was confirmed by periodically monitoring the solution conductivities.

After a steady state was achieved in any run, the following data were obtained:

1. flow rates of concentrating, and diluting, streams to the stack,

2. flow rate in dragout stream by measuring the volume delivered in 30 seconds by the metering pump,

3. concentration of copper and total cyanide in each of the solution holding vessels.

The copper concentrations were determined by atomic absorption spectroscopy after decomposing the cyanides with strong sulfuric acid, neutralizing with ammonia and acidification with acetic acid. Total cyanide was by colorimetric determination of cyanogen bromide with benzidine and pyridine in amyl alcohol according to the procedure described in the appendix.

For a period of an hour after attainment of a steady state, the solution levels in the two vessels were noted and from this data an estimate was made of the net volume transport from one solution to the other. Volume transport in the simulated dragout stream was known from the pump calibration as described above. Except for internal leaks the sole remaining volume transport is by the electroosmotic transport within the stack. This rate is estimated from the algebraic difference between the measured net volume flow rate and the dragout rate.

SECTION V

RESULTS AND DISCUSSION

The purpose of this study was to obtain design parameters for the system. The most important of these is the unit transport capacity for cyanides. It is well known that, for solutions which are sufficiently dilute, the transport capacity of a stack, expressed as equivalents per hour, is directly proportional to the concentration of the diluting stream. This implies that this capacity may be expressed as a parameter which denotes the number of gallons per hour of diluting solution the electrolyte content of which is transported per square foot of membrane.

As indicated in Section IV, we have determined the quantity of cyanides transported per hour in each run. We know also the concentration in the diluting stream to the stack. Dividing the transport rate, in moles per hour, by the concentration, in moles per gallon, yields a parameter for the stack, in units of gallons per hour of diluting solution. When this is divided by the total number of square feet of membrane surface, we obtain the parameter in gph/sq ft, applicable to the design of any stack having the performance characteristics of the stack used in this study.

As indicated in Section IV, the primary solution assays were for copper and total cyanide. Accordingly, the transport parameter is calculated as T_{Cu} from the copper assays and also as T_{Cy} from total cyanide. These appear in Table I. There is no reason to assume that there should be any difference between the two parameters inasmuch as the amount of uncomplexed copper is negligible and that of uncomplexed cyanide is small. Differences which occur may therefore be ascribed to experimental error.

The principal parameters studied were concentrations, voltage and simulated dragout rate. Within each group of tests, viz., 1A-1F, 2A-2E, 3A-3D, 4A-4C, the principal variable is the dragout rate. Comparison of each group with the others reflects the effect of stack voltage and solution composition. The final series, 5A-5B, was primarily to determine the maximum solution concentration and the rate of water transport.

TRANSFER RATE CALCULATION

The transfer rate of the cyanides is measured in the experimental system by operating under a steady rate, i.e., one at which the solution concentrations do not change significantly. The rate of electrolyte transfer by electrodialysis is then equal to the reverse transfer by the metering pump, which simulates the dragout.

In order to determine the transfer rate and the transfer parameters, let:

C_i = the concentration of component i in the concentrating stream in moles/gal
c_i = the concentration in the diluting stream in moles/gal
D = the simulated dragout rate, in gals. per hour
R_i = C/c the ratio of concentrations
Q_i = the transfer rate in moles/(sq. ft.)(hr.)
T_i = the transfer parameter in gal/(sq. ft.) (hr.)
A = the membrane area in sq. ft.

Then we have:

$$Q_i = C_i D/A$$
$$T_i = Q_i/C_i = Q_i R_i/C_i = DR_i/A$$

Subscript i designates the component, for example, copper or total cyanide.

To obtain the most precise determination of the transfer parameter, T_i, it is necessary to determine precisely the concentration ratio, C_i/c_i.

TRANSFER RATES AND CAPACITY

Table 1 shows that a combination of temperatures and high stack voltages favor maximum transfer. Note for example, that in Runs 1 and 2, the third measured value of each run was at the lowest temperature and each yielded the lowest transfer parameter for that run. The transfer rate for Run 2, at 40 volts, is greater than that of Run 1 at 30 volts. However, this is not necessarily ascribable to voltage inasmuch as the temperature was also higher in Run 2 than in Run 1.

In Run 3 we note the effect of higher solution concentration. There is some indication that the transfer capacity is lower at the higher solution concentration at 40 volts for the stack. This is confirmed in Run 5, at 40 and at 30 volts. With the solution in this run at from 52 to 66 per cent of that of the full strength plating solution, the transfer parameter is somewhat lower than it is at lower concentrations for comparable voltage and temperature conditions.

For design purposes consider, as in Run 4, a stack voltage of about 6 volts per cell-pair (allowing about 2 volts for electrode potentials) and a transfer parameter of 8.82 gallons/(sq. ft.) (hr.). The second set of data in this run was obtained at 75°C., which is recommended as the operating temperature. Inasmuch as this data was obtained in concentrated solutions, the transfer parameter is conservative when applied to the more dilute second rinse stage.

The only component concentration, other than copper and cyanide, which was determined in this study, was hydroxyl ion. The activity of this ion is indicated by pH

TABLE 1

CYANIDE RECOVERY BY ELECTRODIALYSIS - SUMMARY OF PERFORMANCE

A. EXPERIMENTAL RESULTS

Run	Temp °C	Amps	Volts	Flow in GPH		Total Cyanide, molar		Copper, atoms/l		pH	
				Dragout	Dil. Stream	Concent. Sol'n	Dilute	Concent. Sol'n	Dilute	Concent. Sol'n	Dilute
1A	30	0.78	30	0.31	300	0.0473	0.00025	0.0120	0.000076	10.8	7.6
B	40	2.6	30	.83	300	.0960	.00153	.0353	.000559	10.5	9.85
C	30	2.4	30	.73	300	.0757	.00334	.0241	.001030	10.5	9.6
D	40	3.2	30	.71	300	.1475	.00169	.0467	.000585	10.55	9.6
E	40	3.7	30	.70	300	.1771	.00234	.0554	.000928	11.05	9.76
F	40	4.0	30	.70	300	.1913	.00238	.0584	.000873	11.35	9.93
2A	45	1.8	30	.65	300	.1199	.00125	.0458	.000373	11.6	9.4
B	42	2.3	30	.66	300	.2075	.00146	.0678	.000551	10.8	10.0
C	40	2.3	30	.66	303	.1637	.00312	.0482	.000924	10.6	9.8
D	47	4.2	40	.68	297	.1992	.00233	.0493	.000566	12.0	9.6
E	46	5.5	43	.82	300	.1453	.00120	.0530	.000771	12.35	9.75
3A	50	7	40	.66	246	.498	.0054	.1164	.0011	9.96	---
B	54	11	40	.86	249	.698	.0137	.1324	.0022	9.83	9.35
C	50	16	40	.84	240	.384	.0091	.0795	.0029	9.80	9.79
D	50	6.5	40	.33	240	.181	.0010	.0511	.0003	9.80	9.64
4A	65	27.5	50	.68	261	2.210	.0133	.700	.0049	13.0	9.23
B	75	30.0	50	.86	225	2.006	.0156	.586	.0044	14.1	10.23
C	65	12	50	.24	240	2.292	.0057	.546	.0009	12.93	9.20
5A	33	30	40	.86	261	3.40	.1310	.887	.0284	14+	---
B	45	34	30	.86	264	2.60	.1360	.690	.0384	14+	13.90

B. DERIVED PARAMETERS

Run	Ratio: Total Cyanide/Cu		Concentration Ratio			% Removal, Dilute		Transport-GPH/Sq Ft		Current Efficiency
	Concent.	Dilute	CN	Cu	OH^-	CN	Cu	CN	Cu	%
1A	2.37	3.31	189.2	265	3000	18.9	27.4	4.53	6.40	21.8
B	2.72	2.74	62.7	63	5	17.3	17.4	4.05	4.07	29.8
C	3.14	3.24	26.7	23	8	6.4	5.6	1.51	1.30	27.0
D	3.16	2.89	87.3	68	9	26.2	16.1	4.83	3.76	38.4
E	3.20	2.52	75.7	60	20	17.7	14.0	4.14	3.28	39.4
F	3.28	2.73	80.4	67	23	18.8	15.7	4.29	3.66	39.2
2A	2.62	2.74	95.9	122	158	20.7	26.4	4.85	6.17	50.7
B	3.06	2.65	142.1	123	6	30.7	27.2	7.18	6.35	70.0
C	3.40	3.38	52.5	52	6	11.5	11.4	2.70	2.68	55.2
D	4.04	4.12	82.7	87	25	18.3	19.8	4.40	4.62	37.7
E	2.74	1.56	121.1	69	398	33.0	18.8	7.72	4.40	25.3
3A	4.25	4.91	92.2	105.8	--	19.3	28.5	4.76	5.46	55.1
B	5.27	6.23	50.9	60.2	3	17.5	20.7	3.42	4.04	64.0
C	4.83	3.31	63.0	27.5	1	22.1	9.7	4.15	1.81	23.8
D	3.54	3.33	181.0	170.5	1	19.3	23.3	4.62	4.36	11.7
4A	3.16	3.25	166.2	143	589	34.1	37.4	8.83	7.64	64.5
B	3.42	3.55	128.6	133.4	7420	50.1	51.1	8.82	9.00	68.0
C	4.20	6.0	402.1	607	5375	39.7	60.1	7.45	11.28	53.3
5A	3.83	4.61	26	31.2	---	8.6	10.35	1.75	2.11	115
B	3.82	3.54	19	17.95	---	6.2	5.9	1.23	1.21	79

from measurements using a glass electrode system. The ratio of hydroxyl activity is calculated from the pH values of the two streams and this ratio is shown in a column of Table 1. It is notable that in Run 4, in which there was free caustic alkali in the concentrating solution, the ratio for hydroxyl is substantially greater than the concentration ratios of copper and total cyanide. This is a consequence of the greater mobility of hydroxyl ions in the anion-selective membranes compared with the mobility of the other anions. This very high ratio of hydroxyl activity is not observed in the other runs of this study, owing probably to buffering effect of the cyanides.

All of the experimental data of Tables 1 and 2 were from analyses of solution samples taken under steady state conditions. Under a steady state the membrane transport of copper and total cyanide is equal to the rate at which these components are transported in the simulated dragout solution. If the volume rate and concentrations are known for this stream which flows from the concentrating to the diluting solution vessel, then we may assume that the transport rates thus determined are equal and opposite to the transport rates of copper and cyanide within the stack.

The system illustrated in Figure 3 performed substantially as anticipated and yielded the data which is summarized in Table 1. Happily the unit capacity for cyanide transport turns out to be markedly improved when the stack voltage is increased. The size of a system is consequently reduced by an order of magnitude below that which was anticipated. This is achieved at the cost of a somewhat greater power requirement which is, however, not excessive in relation to the cyanide and metal values recovered, nor to the saving of capital cost. The economics of the system is discussed below.

There was no difficulty in operating the system continuously and without attention over periods of one week after which it was necessary to remove the copper deposited at

the cathode. The only mechanical difficulty was from a tendency to a slight internal leakage between the two systems. It was determined that this was from a faulty design of the manifold gaskets which tended to collapse around the ports which connect the manifolds and the cells. By control of the pressure differential it was found possible to insure that the slight leakage was always from the diluting stream to the concentrating stream. The rate of this leakage was determined by observing the volume changes of the two solutions without electrical current. A suitable correction was made for this leakage in estimating the electroosmotic flow as described in Section IV. The differential pressure was controlled by control of the solution flow rates. In all runs the concentrating stream rate was 300 gph and the diluting stream flow rate was then adjusted until the required pressure differential was obtained.

CURRENT EFFICIENCY CALCULATION

The current efficiencies are estimated from the total electrolyte transport in equivalents per hour. Inasmuch as the analytical determinations were for the major components only, it has been assumed arbitrarily that, for purposes of estimation, the other electrolyte components are transported at a proportional rate to that of the copper, and that the total sodium content of all solutions is the same in proportion to the total cyanide as it is in the starting solution. Sodium is the only cation in this system, and the total number of gram-equivalents of sodium, estimated in this manner, is therefore a measure of the current efficiency. It is recognized that this method of estimation is inexact, particularly because there is a moderate amount of cyanide loss from the solution because of anodic oxidation. The current efficiencies, when estimated in this way, are therefore being stated conservatively. The basis of calculation of sodium, in epl (equivalents per liter), is as follows:

From NaCN	18 oz/gal x 7.489/49.08	=	2.750
Na_2CO_3	2 oz/gal x 7.489/53	=	.283
NaOH	4 oz/gal x 7.489/40.01	=	.749
			3.782 epl

The total cyanide in the starting solution is:

From NaCN	18 oz/gal x 7.489/49.08	=	2.750
CuCN	16 oz/gal x 7.489/89.56	=	1.338
			4.088 epl

From this the sodium is 0.925 times the total cyanide in epl in the simulated dragout. The product of this factor and the cyanide molarity and dragout rate in liters per hour represents the total electrolyte transport rate. Each gram-equivalent of transport per hour requires 26.8 amperes. The actual number of amperes multiplied by the number of cell-pairs in the stack, 8 in this investigation, is always greater than the electrolyte transport equivalent, and the ratio of these quantities represents the current efficiency.

As efficiency of 100 per cent is achieved only if all membranes are perfectly ion-selective and if there is no leakage of current through the solutions within the manifolds and ports of the stack. In actuality there are current losses from both imperfect ion-selectivity and current leakage. The data obtained in this study does not permit an analysis of the current losses for the present system. The efficiencies are, however, acceptable, particularly in the electrodialysis of solutions in the higher range of concentration. It is in this range that the efficiences are most significant as an index of the power requirement.

ELECTROOSMOTIC TRANSFER OF WATER

The rate of transfer of water by electroosmotic flow is a very important parameter in the first stage of electrodialysis in this system. This is for the reason that the ratio of transport of copper and cyanide to that of water determines the maximum concentration of these components in the solutions which are recovered, or if the concentrating system is from the plating bath, it determines the amount of dilution of the bath from the rinse recovery system. In the second stage of electrodialysis the water transport is negligible because of the much lower concentrations. Results are shown in Table 2.

Table 2

Electroosmotic Transfer of Water

Run No.	Gals/1000 amp-hrs.
3 B	3.2
3 C	8.1
3 D	14.8
4 B	11.5
6 A	5.6
6 B	6.7
6 C	9.8

These results show considerable scatter probably from the difficulty in maintaining the hydraulic balance over the time necessary for measurement with and without current flow. There are also several process variables such as temperature and solution composition which are known to affect the electroosmotic transfer and contribute to the scatter.

Our concern is that if the water which is returned exceeds the combined volume of both evaporation and dragout there will be a problem of controlling the water balance. Within the precision limits of these experiments it appears that for the plating bath containing 16 oz/gal of copper cyanide and 18 oz/gal of sodium cyanide the amount of water returned to the plating bath is about twice the volume of dragout. Evaporation from the surface of the bath in the plating tanks is usually more than sufficient to eliminate this amount of added water. If it is not sufficient some external evaporation may be required.

SYSTEM CHARACTERISTICS AND DESIGN PARAMETERS

The system is fundamentally simple, flexible and stable with respect to process disturbances. The only requirement placed on the operator is to maintain the minimum stream flow rates and the minimum stack voltage. Fail-safe system requirements are satisfied by thermal overload relays for the pump motors, a current-limiting relay on the power line, and protection against excessive temperature rise of the solution.

Because of the very high unit capacity, it is possible to design modular stack components suitable for both small and medium size establishments. The smaller systems may be considerably overdesigned at a relatively low cost penalty. The stack, power supply and control panel may be premounted and assembled. Electrical connection to a three phase power source and piping to the three solution tanks is all that is required for installation.

In any application of this system it is necessary to know the initial bath composition and the maximum concentration allowable in the final rinse. For a two stage rinse system with an equal concentration ratio between stages, this ratio is the square root of the ratio of the concentration of cyanide in the final rinse to that in the plating solution. For example, if the concentration of

cyanide is 100,000 ppm in the plating bath and 10 ppm in the final rinse this, ratio is 10,000:1 and the ratio between stages is 100:1.

It is also necessary to know the rate at which a solution is carried with the work as it enters each rinse tank. Solution carried out of a vessel is termed dragout and solution carried into a tank is termed drag-in. The drag-out of one stage is the drag-in of the next. It may be assumed that the dragout from the plating bath and from each rinse stage are all approximately the same volume.

The dragout rate depends on the amount of work handled, the configuration of the working surface, and the drainage time which is allowed. Plating establishment operators do not generally know exactly what this rate is. It varies somewhat from time to time during operating. Dragout may be estimated from the amount of cyanide required to maintain the bath composition or else by monitoring accumulation of cyanide in the rinse solutions.

These are rules of thumb which may serve as a guide in estimating the dragout if the plating workload is known. Typical amounts of solution removed with each 1000 sq ft of work are as follows:[20]

Vertical parts, well drained	0.4 gallons
Vertical parts, poorly drained	2.0 gallons
Vertical parts, very poorly drained	4.0 gallons
Horizontal parts, well drained	0.8 gallons
Horizontal parts, very poorly drained	10.0 gallons
Cup-shaped parts, very poorly drained	8-24 gallons

If the system is designed for a small or medium-sized plating establishment, it is advantageous to utilize standard power transformers. For example, a standard 208 volt, 3 phase secondary winding, with 120 volts from each leg to ground, may be adapted, by including diodes in the circuit, to deliver 135 volts DC. Allowing for the electrode potentials and for ohmic losses within the stack, each stage will contain 21 cell-pairs.

A stack, such as the WD 6-2, used in this study, contains 0.8 sq ft of effective membrane per cell, or 1.6 sq ft per cell-pair. With the 135 volt DC power supply, such a stack contains 21 x 1.6, or 33.6 sq ft per stage, and it can handle 2.3 gallons per hour of dragout, maintaining a cyanide concentration ratio of 128:1 between the streams. This estimate is based on a transfer parameter of 8.82 gallons/(sq. ft.)(hr.) which is obtained from the data summarized in Table 1, and the calculations, 8.82/128 = 0.069 gallons/(sq. ft.)(hr.), and 33.6 x 0.069 = 2.3 gph.

Based on these assumptions of stack performance and of 128:1 dilution ratio per stage, a membrane area of 33.6/2.3, or 14/6 sq ft, is required for each stage, 29.2 sq ft in all, for each gallon per hour of dragout. With the provision of this amount of stack membrane capacity, the concentration of cyanide and the other substances is sufficiently low in the second rinse solution so that the quality control of the rinse is satisfactory.

The volume of rinse solution in each stage must be sufficient to avoid excessively abrupt changes of concentration. This represents nothing more than normal plating shop practice in counter-current rinsing. In the system which has been developed in this study, the current in each stage of electrodialysis is directly proportional to the solution concentration at that stage. An ammeter in each stage may therefore serve to monitor the concentration and to provide a warning of any tendency to overload the system.

POWER REQUIREMENT AND COSTS

The AC power requirement, allowing for current efficiency, and rectifier and transformer efficiency, is 4.5 KW for each gph of solution dragout of the assumed concentration. Additionally, power is required for three fractional horsepower pump motors. The rectifier energy requirement depends on the total number of equivalents of electrolyte recovered

(plating solution concentration times dragout rate) and on the current efficiency; this is assuming a constant 6 volts per cell-pair. It does not depend greatly on the dilution ratio per stage.

Operating costs for the electrodialysis system, other than those for power, are nominal if the system is well designed. The only moving parts are in the three pumps, and the only normal maintenance is to remove the copper cathodes periodically. Costs, on the basis of one gph dragout at 16 oz/gal copper cyanide, are as follows:

Cost per day, 1 gph dragout, 24 hour operation

Power 120 KWH @ $0.03	$3.60
Labor, operating and maintenance, 1 hr.	4.00
Membrane replacement after 2 yrs. @ $5/sq. ft.	.50
Cost per day	$8.10

The reagents which are recovered represent, at 1 gph for 24 hours, a value of about $49, assuming that there is no bleedoff to maintain the impurity levels. By way of comparison, the cost of chlorination represents a reagent cost of about $2.50 per gallon dragout, or $60 per day at the 1 gph rate which is assumed. Chlorination is, of course, a method of treatment which provides no economic recovery.

The evaporation system of the Pfaudler Division of Sybron Corp., which achieves the same recovery of cyanide as the electrodialysis system developed in this study, costs approximately $30,000 including installation and steam generation facilities. Operating cost of the Pfaudler system, for 1 gph of dragout, using a two-stage rinse system with 100:1 rinse dilution ratio between stages as assumed for the electrodialysis system, is as follows:

Operating Costs per 24 hours

Utilities (steam, power, cooling) @ $0.01 per gallon, 100 gph	$24.00
Labor, $3.00 per man-hour x 2.5 hrs.	7.50
	$31.50

The requirement of steam and cooling water is greatly reduced in the Pfaudler system if additional rinse stages are employed. Estimates such as those above are for purposes of illustration, for comparison of the two systems, and not to indicate the evaporative system which would be utilized in practice.

Whether by electrodialysis or evaporation, the return of all of the cyanide which is removed by the dragout also returns impurities. These must not be allowed to accumulate beyond a harmful level. Sodium carbonate is controlled by occasionally cooling electrolyte, preferably to below ambient temperature and removing crystals. Other impurities are controlled by occasional bleedoff in accordance with plating conditions and requirements. Disposal of concentrated bleedoff may be by electrochemical treatement, chlorination, or by off site treatment. The cost of such treatment is the same for the Pfaudler system as for the electrodialysis.

Both of these systems possess the virtue of eliminating the discharge of dilute cyanide waste and the need for monitoring a waste stream. In the electrodialysis system the stack electric current is proportional to the electrolyte concentration in the diluting stream of each stage. If ammeters are provided, it becomes a simple matter to estimate the dragout load on the rinse system and to control the rinse efficiency.

In addition to the saving in the labor of monitoring a waste stream, there is a saving in the cost of rinse water and of water treatment. However, inasmuch as the impurities contained in evaporation make-up water are retained in the

system and inasmuch as calcium and magnesium in this water tend to produce a sludge with carbonate, it is preferable to use demineralized water for make-up.

The most significant economic advantage of the system developed in this study is the potentially low capital requirement. At the present time the minimum cost, using commercially available equipment, is about $5,000 for the system, exclusive of rinse tanks. It is believed that a much more satisfactory system is possible with stack, pumps, and electrical gear designed specifically for a 2-stage alkaline cyanide recovery in a single stack with six pipe connections at one end plate. Such a system can be manufactured in quantities at a cost which should not exceed $1600. The annual payout of recovered values, based on 240 working days with 1 gph dragout of solution containing 16 oz/gal of cuprous cyanide, after deducting operating costs, is more than $10,000.

This system of electrodialysis is economically sound only if the membrane life is adequate. Membranes used in this study were Ionac MA 3475 as anion-selective and MC 3470, cation-selective membranes. These are products of Ionac Division of Sybron Corporation. They were used in this study for 800 operating hours.

SECTION VI

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SECTION VII

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SECTION VIII

PUBLICATIONS AND PATENTS

U.S. Patent 3,357,823 was awarded to the author, S.B. Tuwiner for the recovery of copper and precious metals using electrodialysis. U.S. Patent 3,674,669 and corresponding applications in Great Britain, Germany, Italy, Canada, Netherlands and Australia is for the system of this report.

APPENDIX

DETERMINATION OF CYANIDE

Cyanogen Bromide with Pyridine and Benzidine in n-amyl Alcohol Method

DISCUSSION

In a weakly acid solution, cyanide is converted to cyanogen bromide by bromine water. After removal of excess bromine, the cyanogen bromide reacts with pyridine and benzidine to form a red-orange color extractable into n-amyl alcohol. The optical density of the n-amyl alcohol layer is then determined on a spectrophotometer after 15 minutes.

REAGENTS

Phosphoric Acid, 2.5%	Dilute 15 ml. of concentrated phosphoric acid (85%) to 500 ml. with distilled water.
Sodium Arsenite, 2%	Weight 2 grams sodium arsenite and dilute to 100 ml. with distilled water.
Pyridine Solution, 30%	Dilute 60 ml. of pyridine with distilled water, add 5.0 ml. concentrated hydrochloric acid and dilute to 200 ml. with distilled water. (Add acid to approximately 100 ml. of distilled water in a 200 ml. volumetric flask, mix and add pyridine, mix and dilute to 200 ml.) Prepare daily.

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Benzidine Hydrochloride, 1.5%	Weight 1.5 Gm. benzidine hydrochloride and make to 100 ml. with distilled water. Add a few drops of 1:1 HCl to assist solution of the material if necessary. Prepare daily.
Bromine Water, Saturated	Add several drops of bromine to 100 ml. distilled water and shake vigorously for 10 to 15 seconds. Since the solution loses strength with time, due to volatilization of bromine, it is advisable to resaturate with bromine just prior to use. Store in a glass bottle in a relatively cool area.
Stock Cyanide Solution "A"	Dissolve 0.195 grams of NaCN, reagent grade, in distilled water made alkaline with NaOH solution to pH 11. Dilute to one liter with distilled water. 0.1 gm. CN^- per liter
"B"	Dilute 10 ml. of Solution "A" to one liter with distilled water made alkaline with NaOH solution. 0.001 gm. CN^- per liter
"C"	Dilute 10 ml. of Solution "B" to 100 ml. with distilled water made alkaline with NaOH solution. 1 ml. = 0.1 ppm CN^-

(Standard solutions should be prepared fresh at frequent intervals, maximum weekly and stored in a cool place.)

n-amyl Alcohol, C.P. — Used as received.

Sodium Sulfate, Anhydrous, Crystal — Used as received.

PROCEDURE

Measure a 100 ml. sample and place in a 250 ml. separatory funnel.

Measure 100 ml. of distilled water made alkaline with NaOH solution into a 250 ml. separatory funnel. (Blank)

Standards for preparation of a standard curve.

Add distilled water made alkaline with NaOH solution to pH 11.0 to three 250 ml. separatory funnels; 95 ml., 90 ml. and 80 ml. Now add 5 ml., 10 ml. and 20 ml. aliquots of the "C" Standard Stock Solution to the funnels by pipette. Equal to one part per billion per ml. when diluted to 100 ml.

Carry standard samples, blank and unknowns, through the whole procedure.

Add 4 ml. phosphoric acid solution to each funnel and mix. Check the pH at this point. If the pH is above 3, using pHydrion paper, add an additional milliliter of phosphoric acid. Use a 25 ml. Mohr Pipette.

Add bromine water dropwise until a distinct pale yellow color is seen and mix. Usually one to three drops are sufficient, but more may be necessary for high samples. Use a 2 ml. transfer pipette.

Add 25 ml. n-amyl alcohol, preferably by buret, to each flask.

Add 1 ml. benzidine solution to each flask, stopper and shake vigorously for about 15 seconds.

Add 10 ml. pyridine solution to each flask. (Do not pipette by mouth.)

Begin timer.

After 15 minutes, draw off the lower aqueous layer and discard.

Now add the n-amyl alcohol layer to a 125 ml. erlenmeyer flask containing roughly 20 grams anhydrous sodium sulfate (one level tablespoon). Swirl to remove water.

Transfer to cuvettes and read on a spectrophotometer at a wave length of 475 mu, using the blank as a reference blank.

NOTES ON TRACE CYANIDE ANALYSIS

CONTAMINATION - The concentrations of Cyanide in solutions that this procedure is designed to detect and analyze are in the 10 parts per billion range. Carlin mill solutions contain 0.25% Cyanide. Any contact with mill solutions via hands, or interchange of glassware would result in high Cyanide assays (incorrect because of contamination).

Glassware used for this procedure must not be used for any mill solutions under any circumstances.

PIPETTING - All pipetting must be done by use of the rubber bulb. Remember that cyanide is a poison and mouth suction on a pipette is a dangerous and hazardous technique.

A stream of distilled water should be forced through each pipette used, immediately after use. Do not permit solutions of unknown or higher concentrations to dry on the inside of pipette. Resulting contamination would give high or erratic assays.

In pipetting standards or aliquots, one technique is very helpful to avoid contamination. Fill the pipette with the solution to be pipetted and discard three times. Fill the fourth time, wipe the outside of the pipette with a tissue and drain to the line. Then transfer into the flask the aliquot is intended for.

PRESERVATION OF SAMPLES - Since most cyanides are very reactive and unstable, analysis should be made as soon as possible after sampling. If the sample cannot be analyzed immediately, add NaOH to raise the pH to 11.0 or above and store in a cool place.

CLEANING GLASSWARE - Clean pipettes in chromic acid cleaning solution daily. Rinse well with distilled water and air dry in dust-free area.

Glassware which is contacted by n-amyl alcohol should be washed in hot alconox detergent solution. Includes 250 ml. buret, separatory funnels, 125 erlenmeyer flasks, cuvettes and beakers used to drain aqueous from separatory funnels. Rinse well with distilled water.

STANDARDS - Standards are not necessary for each set of unknown determinations. Three points on the curve are run with each set for contamination control.

SECTION X

GLOSSARY

Anion-selective membrane A membrane which is considerably more permeable to anions than to cations. Ideally such a membrane should prevent cation passage and permit free electromigration of anions

Cation-selective membrane A counterpart of the above. It permits cation electromigration and restricts the flow of anions.

Cell The space, usually narrow, between two membranes and enclosed within a frame

Concentrating solution, concentrating stream The solution or stream which becomes more concentrated in electrodialysis

Diluting solution, diluting stream The diluting counterpart of the above

Electrodes Electrically conducting sheets or plates within, or a part of, the end plates of en electrodialysis stack. One is an anode and the other a cathode.

Electrode rinse cell, electrode rinse stream The cell, or solution stream of an electrode. The electrode rinse stream contains the products of the electrode reaction

Electrodialyzer A system for transport of electrolyte from a diluting stream to a concentrating system by the electromigration of cations through a cation-selective membrane and of anions through an anion-selective membrane. The term is applied either to the stack or stacks alone, or to the entire system including pumps and rectifier.

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Electrodialysis A method based on the use of one or more electrodialyzers

Electroosmotic flow Transport of water or solution through ion-selective membranes under the influence of an electric field

Electromigration Migration of ions through an ion-selective membrane in an electric field

Membrane A barrier which is selectively permeable to ions or molecules. Those of interest are polymer sheet materials which are useful in electrodialysis

Polarization A phenomenon which limits the flow of ionic current. One form is concentration polarization, which occurs because of electrolyte depletion at a membrane-solution interface.

Ratio of concentration or dilution A ratio of concentration of a component in the concentrating and diluting streams or between rinse stages

Stack, or electrodialyzer stack An assembly of membranes, frames and spacers with end plates and electrodes. The term derives from the parallel stacked arrangement of the components.